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THERMO-MECHANICAL ANALYSIS OF OXIDATION PROTECTED CARBON-CARBON COMPOSITES

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13. ABSTRACT (*Maximum 200 words*)

The AFOSR oxidation-protected C-C composite program is focused on developing and verifying mathematical models predicting the thermomechanical properties of exposed carbon-carbon composites. These models will be utilized to make judgements on the merits of both current and future materials concepts for oxidation resistance. These efforts are focused on the understanding of the formation and growth of damage within these materials, and on the influence of oxidation protection constituents on the overall carbon-carbon material system. Models will be used to investigate the effects of inhibitors, microcrack patterns, fiber coatings, surface coatings and matrix replacements on effective thermomechanical properties of carbon-carbon materials. The result of these models will allow the quantification of effective crack management strategies to improve the overall performance of these materials. Parallel efforts in this program include an experimental portion for the quantification of microcracks within the material and a variety of thermomechanical tests on specimens with and without coatings and inhibitors. Different material systems will allow a full range of constituent and processing variables to be studied. Results of these experiments will be compared to the predictions of the mathematical models in order to suggest improved design methods for carbon-carbon material systems.

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PREFACE

This report presents the results of a study performed under contract F49620-92-C-0024 during the period of February, 1992 to February, 1993. The program manager for the Materials Sciences Corporation was Dr. B. Walter Rosen. Contributions to this program were made by Dr. Zvi Hashin, Dr. Mark Jones, and Mr. Thomas Cassin. The technical monitor for AFOSR is Dr. Walter Jones.

APPROVED

B. Walter Rosen
Program Manager

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OBJECTIVE

Efforts in the AFOSR oxidation-protected C-C composite program are focused in three central areas. These areas are: analytical methodology development, experimental characterization/validation of material morphology, and substrate/coating crack management. The first two areas are being performed as closely integrated tasks. The focus is on the development of analytical methodologies, with a priori damage quantification, to characterize the thermomechanical properties of coated carbon-carbon composites. Experimental data are being used to identify initial and progressive material damage states. The characterization of several different material systems will allow a full range of constituent and processing variables to be studied. The results of these tasks will be used in the third area of study which is provided to understand and control the initiation and progression of cracks in protective coatings.

Two approaches have been identified to understand the formation and growth of damage within these materials. The first, Micromechanics of Oxidation Protection (MOP) models are being developed to enhance the capabilities of utilizing constituent properties for predicting bundle and interstitial matrix region properties, composite unit cell properties and structural properties. These models will be used to investigate the effects of inhibitors, microcrack patterns, fiber coatings, surface coatings and matrix replacements on effective thermomechanical properties of carbon-carbon materials containing realistic cracks and disbonds representative of the material as-manufactured and after thermal exposure. The second approach, termed Crack Management (CM), is being developed to track the damage progression in protective coatings allowing the determination of the critical topological energy states that exist in the coated materials. The result of this development program will allow for the quantification of effective crack management strategies improving the overall performance of these materials.

A second phase experimental program is planned to provide experimental data for correlation studies with the analytical models. The results of the experiments will be compared to the predictions of the mathematical models in order to suggest improved design methods for carbon-carbon material systems. Crack patterns, crack densities and crack opening displacements will be used as criteria for performance. These models will be utilized

to make judgements on the merits of both current and future materials concepts for oxidation resistance.

ANALYTICAL DEVELOPMENT

BACKGROUND

The temperature induced changes encountered in the manufacturing process of carbon-carbon (C-C) composites produce significant tensile stresses which in turn produce cracks in the C-C. Typical cracks observed [1] are: (a) randomly oriented cracks in the graphitic matrix in which the fiber bundles are embedded; (b) axial cracks (parallel to fiber direction) in the fiber bundles; (c) cracks in the fiber coating in the event of fiber protection by coating. In addition, there are (d) initial voids in the matrix.

An important aspect of oxidation protection of C-C composites is the filling out of internal cracks and voids with SiC. The purpose of this procedure is the prevention of oxidation of the free surfaces of the cracks and voids. It is well known that cracks and voids in homogeneous materials which are subjected to uniform temperature changes do not give rise to thermal stresses. The cracks and pores in the interstitial matrix are sufficiently large with respect to microstructure dimensions to regard them as being situated in a homogeneous material. This is also true, though to a lesser extent, for the cracks in the fiber bundle. Thus, uniform temperature changes would not produce thermal stresses of any significance near these cracks and voids. The situation becomes entirely different when these voids are filled out by SiC for now they become inclusions in a matrix and since the Coefficient of Thermal Expansion (CTE) of SiC and the matrix are different, temperature changes will produce internal stresses. Tensile thermal stresses at the inclusion/matrix interface may produce separation of inclusions from the matrix, which would result in a renewed free surface o the graphitic matrix with consequent oxidation. This motivates the analysis of the thermal stresses near and inside the various inclusions formed in order to investigate the effectiveness of such an oxidation inhibition method.

APPROACH

The analytical portion of this program involves the development and implementation of two separate material design methodologies. The first, micro-mechanics of oxidation protection (MOP), is concerned with the scale of pores, matrix cracks, inclusions resulting

from filling out the scale of pores, fibers, etc. Additionally, MOP also determines if the effects of oxidation protection on this scale are efficient. For example, what stresses occur at inclusion interfaces, and to what extent do these stresses cause separation of the inhibitor from the substrate. The second, crack management (CM), seeks to identify the cause and effect of surface and sub-surface crack patterns. The motivation of CM is to understand and control the formation and accumulation of potentially destructive material flaws.

MODULAR ANALYSIS METHODOLOGY

The development of a modular analysis scheme is essential to the utility and efficiency of a uniform design method. The separate modules, as shown in Figure 1, have been identified to characterize the behavior of oxidation protected carbon-carbon materials. The analytical development of a portion of these modules are already pre-existing. The remainder of the analytical characterizations, particularly dealing with thermally induced stresses, need to be developed. The fundamentals of these new methodologies are presented in the following paragraphs. The result of this compilation will be a FORTRAN computer code which will allow parametric investigations of various material architectures.

THERMAL STRESS ANALYSIS

There exists a large amount of literature on the stress analysis of inclusions embedded in large bodies with remote uniform strain or stress prescribed. See, e.g., [2]. By contrast, there is only scant literature on thermal stress analysis of inclusions. In the course of present research, we have devised a novel method of thermal stress analysis which converts the thermoelastic problem into an isothermal elasticity problem. The general result is as follows: consider an elastic body of material 1 in which there are embedded elastic inclusions of material 2. The composite body is subjected to a uniform temperature change ϕ and the surface displacements are prescribed as $u(S) = u^o$.

Let the thermoelastic solution in the phases 1, 2 be denoted $u^1(x)$, $u^2(x)$. Then the thermoelastic solution can be expressed as

$$u^1 = \tilde{u}^1 + \beta x$$
$$u^2 = \tilde{u}^2 + \beta x \qquad (1)$$

where $\tilde{u}^1$, $\tilde{u}^2$ are phase displacements for the isothermal elasticity problem with displacement boundary condition

$$\tilde{u}(S) = u^0(S) - \beta x (S) \qquad (2)$$

The second rank tensor β is defined as

$$\beta = -(C^2 - C^1)^{-1} (\Gamma^2 - \Gamma^1) \phi \qquad (3)$$

where C is elastic moduli tensor and Γ is thermal stiffness tensor which define the thermoelastic stress strain relations. Thus

$$\sigma = C\epsilon + \Gamma\phi$$
$$\Gamma = -C\alpha \qquad (4)$$

Filled Matrix Crack

This refers to cracks (a) above which are filled out with SiC. The cracks will be modeled as very flat oblate spheroids of radius a and small diameter 2c, Figure 2. The problem then is to find the thermal stresses in and near such a spheroidal inclusion when the temperature is uniformly changed by an amount ϕ.

On the basis of the previously summarized general solution, the problem can be solved in terms of the well known solution for a spheroidal inclusion with remote uniform strain. Thus, the strain $\epsilon^{(2)}$ in the inclusion for the present problem is given by

$$(SS^1C^2 - S + I)\, \epsilon^2 = S(S^1C^2 - I)\, \beta + \alpha^1 \varphi \qquad (5)$$

where

S - Eshelby Tensor

S^1 - Matrix Compliance

C^2 - Inclusion Stiffness

ϵ^2 - Inclusion Strain

I - 4th Rank Unit Tensor

α^1 - Matrix Thermal Expansion Tensor

For isotropic matrix and inclusion, these equations assume the form

$$\left[\frac{1}{3}\left(\frac{k_2}{k_1}-\frac{G_2}{G_1}\right)S_{ijmm}d_{kl}+\left(\frac{G_2}{G_1}-1\right)S_{ijkl}+I_{ijkl}\right]\epsilon_1^2 = \left[\frac{k_2\alpha_2-k_1\alpha_1}{k_1}S_{ijmm}+\alpha_1 d_{ij}\right]\varphi \qquad (6)$$

where k and G are bulk and shear modulus, respectively.

A sample calculation has been performed for the case of a SiC inclusion of aspect ratio c/a = 0.1 which is embedded in ATJ graphite isotropic matrix. Note that the tensile ultimate stress of such a matrix is only 500 psi. It was found that for a temperature cooldown of 2000°F, the stress normal to the surface of the inclusion varies within the limits 880, 8300 psi. It follows that the inclusion will separate from the matrix on its entire surface and thus the oxidation protection fails.

Filled Bundle Crack

Bundle cracks (b) observed are long cracks parallel to the fibers which are assumed to be cylindrical with generator in fiber direction and flat elliptical in the transverse plane of the bundle, Figure 3. It is further assumed that the crack length is large enough compared to fiber diameters so that it may be assumed that the material surrounding the crack is transversely isotropic with the effective properties of the unidirectional bundle material. The crack is now filled out with isotropic SiC inhibitor material. Thus the problem activity is modeled as the thermoelastic analysis of an isotropic elliptic cylinder which is embedded in a transversely isotropic matrix.

Note that the general solution for the thermal inclusion problem as given by (5) is applicable to the present problem with the following interpretation.

- S^1 - Transversely isotropic compliance tensor of "matrix" (unidirectional bundle)
- C^2 - Isotropic stiffness tensor of SiC
- α^1 - Transversely isotropic TEC of "matrix"
- S - Eshelby tensor for elliptical cylindrical region in transversely isotropic matrix

The major difficulty is evaluation of the components of S and this has been carried out on the basis of a method described in Mura [2].

Once $\epsilon^{(2)}$ has been determined for (S), the inclusion stresses are given by

$$\sigma^2 = C^2\epsilon^2 + \Gamma^2\varphi \tag{7}$$

We have performed a sample calculation of a SiC filled crack in a bundle consisting of T300 fibers embedded in ATJ graphite isotropic matrix for fiber volume concentration $V_f = 0.60$. For a cooldown of 2000°F, we obtained compressive transverse stresses in the SiC and an axial tensile stress which varies between 350 - 380 ksi for various aspect ratios of the ellipse. Since the ultimate tensile stress of SiC is about 45 ksi, this implies that the SiC will fail by transverse cracking in many places. The filled SiC crack will literally shatter into small pieces and thus the inhibitor is ineffective.

Interphase Failure

Graphite fibers are frequently coated for reasons of surface protection. The integrity of this protection depends on the ability of the fiber coating, from now on referred to as interphase to withstand the internal stresses in the interphase. We have considered the case of very thin interphase and have been able to derive novel results for the interphase stresses on the basis of the Composite Cylinder Assemblage (CCA) model and the Generalized Self Consistent Scheme (GSCS) model (see, e.g., [3]). It has proved possible to evaluate the interphase stresses solely in terms of effective thermoelastic properties of the composite.

We are primarily interested in the interphase stresses due to temperature change. A sample calculation for the case of T300 fibers, embedded in ATJ graphite matrix at 0.60 volume fraction and a temperature cooldown of -2000°F, assuming reasonable interphase properties has given the following results for interphase stresses.

$$G_{rr} = 1.37 \text{ ksi}$$

$$\sigma_{\theta\theta} = 7.27 \text{ ksi}$$

$$\sigma_{zz} = 13.1 \text{ ksi}$$

It is believed that the axial stress σ_{zz} will fail the interphase.

CONCLUSIONS

It appears that temperature cooldown of the order of -2000°F produce severe thermal stress which will lead to separation of inhibitor (SiC) from the internal surface (crack) which it is suppose to protect. Similarly, such temperature drops will probably fail the interphase between fibers and matrix.

Thought must be given as to how such stresses can be reduced.

EXPERIMENTAL PROGRAM

PROGRAM OBJECTIVE

The objectives of the experimental portion of this program are to provide the micro-structural characterization data and thermo-mechanical test data necessary to support and validate the mathematical models being developed at MSC.

BACKGROUND

The primary contributor to the experimental program is Prof. Steve Yurgartis of Clarkson University, Potsdam, NY. Prof. Yurgartis has an 18 month contract from MSC to perform micro-structural classification and quantification of the processing cracks, and other damages, commonly found in carbon-carbon substrates. In addition, specimen preparation and image analysis techniques will be developed to allow characterization and quantification of the crack network in the external CVD coating systems. Other program participants include Materials Suppliers: Hitco and Rohr for carbon-carbon substrates and Chromalloy and BFGoodrich for CVD coatings. Thermo-mechanical testing of the coated and uncoated materials will be performed on an as-needed basis.

PROGRAM MATERIALS

As originally proposed, the experimental portion of MSC's program would make use of substrates and coated coupons manufactured under MSNW's Wright Labs. Alternate Inhibitor program. However, the residual materials from the MSNW program were never released, and it became necessary for MSC to initiate procurement of alternate substrates and coatings. These efforts have been successful, and two groups of material, representative of the current state-of-the-art in oxidation resistant carbon-carbon have been procured. The history of these materials is given in the following sections:

Hitco/Chromalloy.

The immediate need of the experimental program was the procurement of materials for use by Clarkson in developing and refining their specimen preparation and damage quantification techniques. To this end, a number of coated oxidation coupons from a joint Hitco (CC137E substrate) and Chromalloy (RT42A coating) materials development program were provided, gratis. Two of these coupons were transferred to Clarkson for examination, the results of which are described in detail in Clarkson's first two quarterly reports.

Rohr Inc.

While satisfying the immediate needs of the Clarkson contract, the Hitco/CRT coupons represented only one fixed oxidation protection system (CC137G/RT42A) with no opportunity for pre-coating examination and little chance of substrate variations. The need for an alternate substrate source was subsequently reinforced by Hitco's decision to cease all carbon-carbon R&D activities.

Contact was made with Rohr Inc., San Diego, CA, with regard to fabrication of some specialty substrate materials, representative of a variety of alternate oxidation protection concepts for inclusion in the program. During discussions, it was noted that Rohr had a stock of pre-fabricated IR&D materials which included many of the oxidation protection concepts under consideration. Availability of these materials offered an excellent opportunity to investigate micro-structure property relationships, and validate the MSC analytical models without the expense of a specialty material manufacturing program. Arrangements were made to procure small quantities of several of these materials. Rohr was also able to supply data sheets with moduli and strength values for most of these materials. A description of the Rohr materials and their characteristics are given in Table 1.

CLARKSON UNIVERSITY

At the time of writing Clarkson are approximately half-way through their assigned contract. As previously mentioned, MSC has supplied Yurgartis with two shipments of material for evaluation. Shipment #1 consisted of 2 coated coupons (CRT/Hitco) intended for

use as "dummy" coupons for development of a coating crack measurement technique. Shipment #2 consisted of small 1x1 inch pieces from the five Rohr substrates listed in Table 1.

The major findings from the Clarkson study may be summarized as follows:

1. The preferred orientation for process-induced substrate micro-cracks was parallel to the fiber orientation and perpendicular to the plane of the fabric. Longitudinal matrix cracks perpendicular to the fiber axis were not observed (Figure 4).
2. Three types of coating cracks were identified propagating outward from the substrate: Type 1 - Those constrained within the first coating layer; Type 2 -Those that penetrated more than one layer; and Type 3 - Those that penetrated the whole coating thickness (Figure 5).
3. For Type 3 Cracks the average spacing was found to be approx. 0.8 mm, and the average spacing for all cracks was found to be approx. 0.2 mm. The Type 3 (through-thickness) crack spacing corresponds to about 50% of the yarn diameter for the 3k T300 8 harness satin weave fabric in the substrate (Figure 6).

Preliminary examination of the Rohr substrates (Figure 7) indicates that a wide range of micro-structural characteristics are contained within these materials. Examination of the data sheets suggests that these characteristics are reflected in a wide range of thermo-mechanical properties.

FUTURE WORK

It may be seen from Table 1 that the Rohr materials procured in support of this program reflect a range of material styles and oxidation protection concepts. Among the parameters represented are:

Inhibitor Level

Inhibitor Type

Weave Style

Fiber Type (Heat Treat)

Fiber Orientation

This array of parameters offers an excellent opportunity to gain a better understanding of the substrate/coating interactions, with a view to postulation of possible crack management strategies.

The immediate action plan calls for detailed thermal expansion testing of the five substrate panels in the uncoated state up to 1500°C. After CTE determination, each of the five substrate material specimens will be sub-divided into multiple pieces for application of two coating variants - Table 2. One of these coating systems will be SiC, and the other will be co-deposited SiC/BxC system. Previous work on coatings of this type has shown that the BxC layer has very different crack characteristics compared to the straight SiC layers (Clarkson Report #2). Thus, coating crack characteristics become another parameter for introduction into the analysis.

Post-coating crack quantification at Clarkson should seek to prove either of three hypotheses:

1). The cracking process is governed by first-order material parameters which may be identified and controlled.

or

2). The cracking process is governed by second-order material parameters which have yet to be identified.

or

3). The cracking process is governed by chaotic events outside the range of normal control.

REFERENCES

1. Clarkson University Quarterly Progress Reports, 1992-1993.
2. Mura, T., "Micromechanics of Defects in Solids", M. Nighoff, 1987.
3. Hashin, Z., "Theory of Analysis of Composite Materials - A Survey", J. Appl. Mechs., 50, 481-505, 1983.

Table 1. The Rohr substrates procured in support of this program represent a variety of material styles and oxidation protection concepts with a wide range of thermo-mechanical properties.

Panel I.D.	Material Description	Tensile Modulus, Msi	Shear Modulus, Msi	Strength, Ksi	Porosity, v/o	Fiber Fract. v/o
1D	8 Harness Satin Weave T300 Fiber (2650°C Heat Treat) Uninhibited	23	0.8	42.6	4.7	63
20D	8 Harness Satin Weave T300 Fiber (2150°C Heat Treat) Uninhibited	18.3	1.4	37.8	0.8	71
31H	8 Harness Satin Weave T300 Fiber (2150°C) V. High Inhibitor Level	8.5	0.5	10.5	21.1	42
62H	8 Harness Satin Weave T300 Fiber (2150°C) SiC Whiskers	11.9	1.5	46.0	2.6	51
137G	Plain Weave T300 Fiber (2150°C) Medium Inhibitor Level	11.5	-	-	-	43

All data measured by Rohr

Table 2. AFOSR material disposition includes thermo-mechanical evaluation and micro-structural characterization.

Panel I.D.	Panel Size	Coating Plan	Post-Coat Disposition
1D	3x1 ins.	Cut into 2 of 1x1's 1 pc. - Coating A 1 pc. - Coating B	Send to Clarkson for metallography and crack patterns No post-coat mechanicals
20D	3x1 ins.	Same as 1D above	Same as above
31H	9x1 ins.	Cut into 4 pcs: 2 of 3x1's, 2 of 1x1's 1 pc. each Coating A 1 pc. each Coating B	Small pcs. to Clarkson Larger pcs. for CTE and Moduli
62H	9x1 ins.	Same as 31H above	Same as above
137G	6x8 ins.	Cut into 10 pcs: 4 pcs. axial orientation 6 pcs. bias orientation	Same as above

Coating A = 10 mils Sic Coating B = 10 mils SiC/BxC

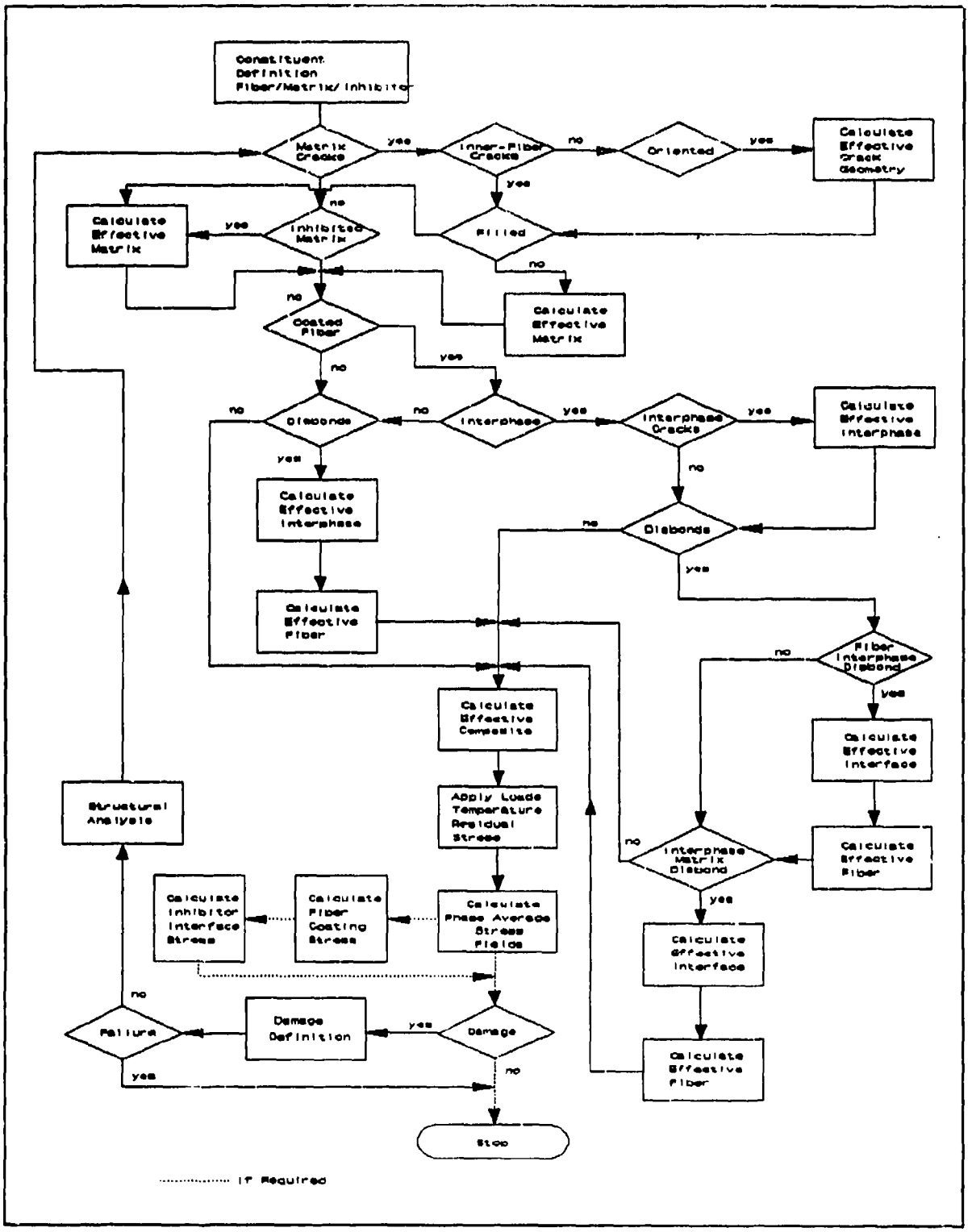
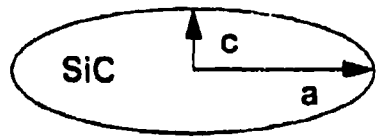


Figure 1 - ORCC DAMAGE CHARACTERIZATION FLOWCHART



Graphitic Matrix

Figure 2. Spheroidal SiC Inclusion.

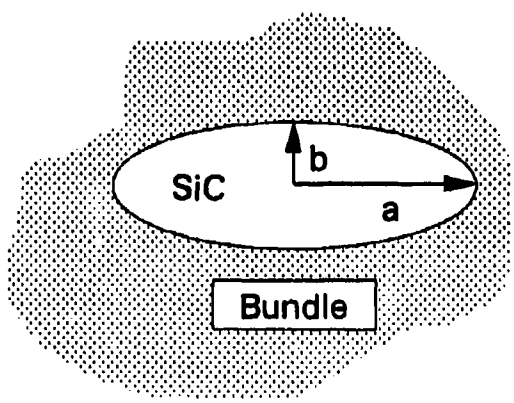
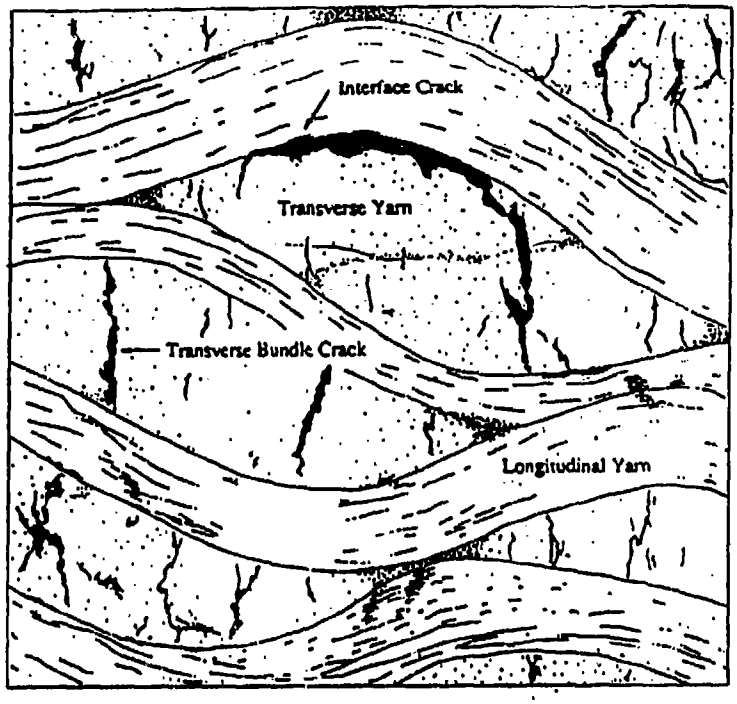


Figure 3. Filled Out Crack In Bundle.



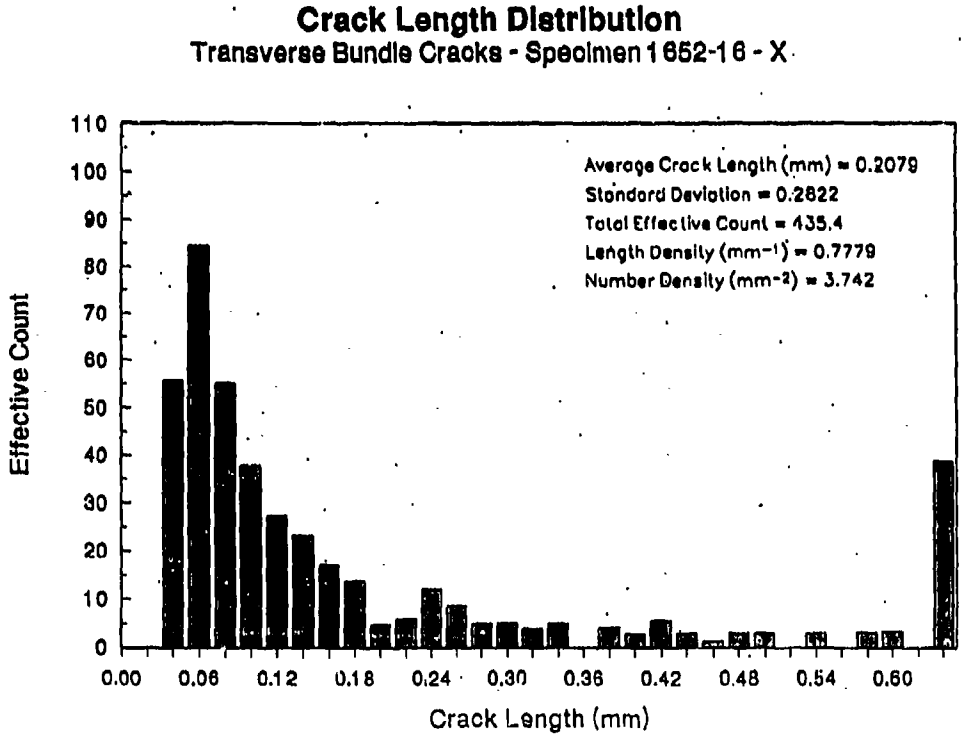


Figure 4. The substrate crack pattern reflected a preponderance of transverse bundle cracks of 0.2 mm. average length.

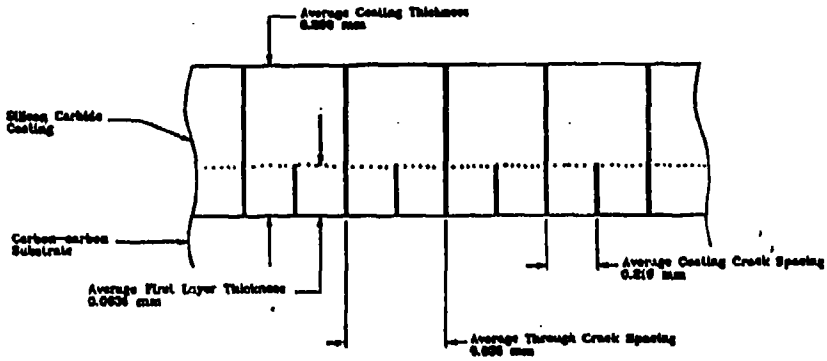


Figure 5. The external CVD SiC coating contained three crack types: Type 1 - single layer cracks; Type 2 - Multi-layer cracks; and Type 3 - Through cracks.

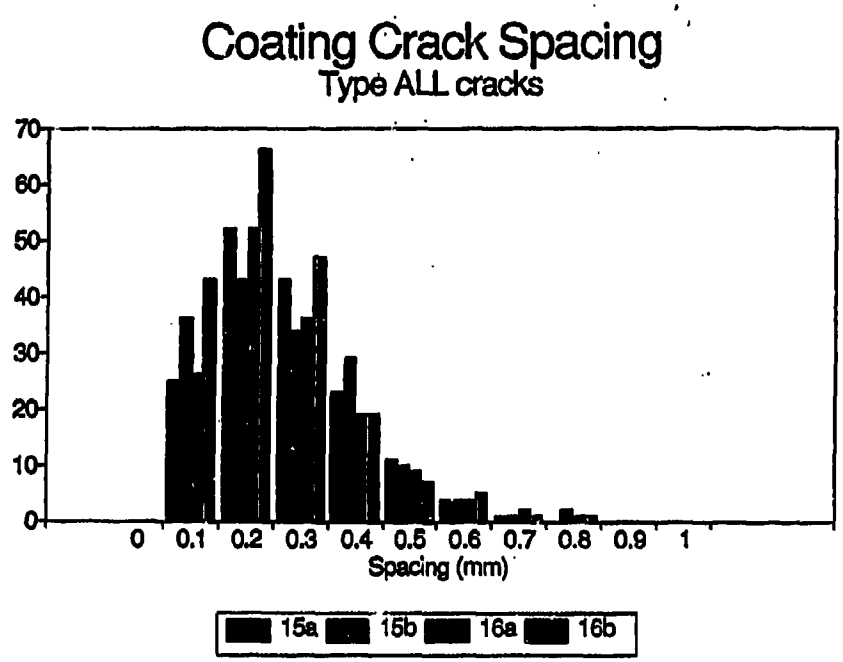


Figure 6. **The external coating crack spacing for the Hitco/Chromalloy materials averaged out at around 0.2 mm for all types.**

A). Rohr uninhibited - satin weave

B). Rohr inhibited - plain weave

Figure 7. The recently received Rohr substrates represent a number of different micro-structural characteristics.